

Debye-Hückel-Bjerrum theory for charged colloids

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We formulate an extension of the Debye-Hückel-Bjerrum theory [M. E. Fisher and Y. Levin, *Phys. Rev. Lett.* **71**, 3826 (1993)] to the fluid state of a highly asymmetric charged colloid. Allowing for the formation of clusters consisting of one polyion and n condensed counterions, the total Helmholtz free energy of the colloidal suspension is constructed. The thermodynamic properties, such as the cluster-density distribution and the pressure, are obtained by the minimization of the free energy under the constraints of fixed number of polyions and counterions. In agreement with the current experimental and Monte Carlo results, no evidence of any phase transition is encountered.

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I. INTRODUCTION

The technological importance of charged colloidal suspensions can not be overemphasized. One comes across these important systems in fields as diverse as the chemical engineering and the environmental science. Many water-soluble paints contain charged colloidal suspensions as a main ingredient. In this case the problem of great industrial importance is to stabilize the suspension against the flocculation and precipitation. On the other extreme is the constantly growing environmental necessity of cleaning contaminated water. For this it is essential to find the most effective way of precipitating the (usually) charged organic particles dissolved in the water.

From the theoretical perspective the problem of strongly asymmetric electrolyte solutions is extremely difficult to study. The long-ranged nature of the Coulomb force combined with the large charge and size asymmetry between the polyions and the counterions and coions makes it impossible to use the traditional methods of liquid-state theory. At high volume fractions the suspension will crystallize, that is, the polyions will become arranged in the form of a lattice. The solid state provides a major simplification of reducing the many-polyion problem to that of one polyion inside a Wigner-Seitz (WS) cell [1]. Unfortunately, at low densities, or in the presence of a simple electrolyte, the suspension becomes disordered and the WS picture is no longer valid [2]. A new strategy must be tried.

The Debye-Hückel-Bjerrum theory (DHBj) [3] was quite successful in explaining the behavior of symmetric electrolytes. The Bjerrum's concept of association of oppositely charged ions into dipolar pairs [4] served to correct the Debye-Hückel (DH) linearization of the non-linear Poisson-Boltzmann equation [5]. Taking into ac-

count the dipolar solvation energy made the coexistence curve produced by the DHBj theory [3] become in excellent agreement with the Monte Carlo simulations [6]. The large surface charge of a polyion suggests that the cluster formation should be even more important in the case of polyelectrolytes. In the present work we shall explore to what extent the counterion condensation influences the thermodynamic properties of a polyelectrolyte solution. The DHBj theory will be extended to treat the fluid state of a charged colloidal suspension.

II. DEFINITION OF THE MODEL

We shall work with the primitive model of polyelectrolyte (PMP) [7]. The system will consist of N_p polyions inside a volume V . The polyions are modeled as hard spheres of radius a with a uniform surface charge density

$$\sigma_0 = -\frac{Zq}{4\pi a^2}, \quad (1)$$

where Z is the polyion valence (number of ionized sites) and $q > 0$ is the charge of a proton. To preserve the overall charge neutrality of the system, ZN_p point-like counterions of charge $+q$ are present. The solvent is modeled as a homogeneous medium of dielectric constant D . Due to the strong electrostatic interaction between the polyions and the counterions, we expect that the asymmetric polyelectrolyte will be composed of clusters, with density ρ_n , consisting of one polyion and $1 \leq n \leq Z$ associated counterions, as well as bare polyions of density ρ_0 and free (unassociated) counterions of density ρ_f . The conservation of the total number of polyions and counterions leads to two conservation equations,

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$$\rho_p = \sum_{n=0}^Z \rho_n , \quad (2)$$

and

$$Z\rho_p = \rho_f + \sum_{n=0}^Z n\rho_n , \quad (3)$$

where $\rho_p = N_p/V$ is the total density of polyions (associated or not).

All the thermodynamic properties of the system can be determined once the free energy is known. The Helmholtz free energy can be split into two parts, the electrostatic and entropic. The electrostatic terms are due to the inter-particles interactions and can be attributed to the polyion-counterion, the polyion-polyion, and the counterion-counterion interactions. All the electrostatic interactions will be evaluated using the DH theory [5]. This is motivated by the former success of the theory when it was applied to symmetric electrolytes. In principle, the linear DH theory is satisfactory only for low densities and high temperatures. However, once the concept of clusters is introduced, the validity of the DHBj theory is extended into the nonlinear regime [3]. The linear structure of the DHBj theory insures its internal self consistency, a problem which is intrinsic to many of the nonlinear theories of electrolyte solutions [8].

We shall assume that the effect of the counterion condensation is to renormalize the polyion charge. Thus, the effective surface charge of a n -cluster is

$$\sigma_n = -\frac{(Z-n)q}{4\pi a^2} = \sigma_0 \frac{Z-n}{Z} . \quad (4)$$

All the nonlinearities related to the internal degrees of freedom of the clusters will be included in the entropic terms. In a previous work [7a] we have considered that the bounded counterions condense onto the surface of the spherical polyion. Although less realistic, this assumption has allowed us to obtain closed analytical expressions for the entropic contribution. In the present work, however, the intra-cluster interactions will be treated using a local-density functional theory, so that the correlations between the bound counterions are explicitly taken into account. These correlations effects can be disregarded only when the concentration of counterions is not too high, a condition which may not be fulfilled in the close vicinity of a highly charged polyion. We now proceed to describe each one of the contributions to the Helmholtz free-energy density $f = -F/V$.

III. THE POLYION-COUNTERION INTERACTION

The *polyion-counterion* contribution is obtained using the usual DH theory applied to a n -cluster of effective

surface charge σ_n inside the ionic atmosphere [7a]. Consider a n -cluster fixed at the origin, $r = 0$. Due to the hard-sphere exclusion, no counterions will be found inside the region $r < a$, that is,

$$\rho_q(r < a) = 0 . \quad (5)$$

Outside the spherical polyion, $r \geq a$, the cluster-counterion correlation function is approximated by a Boltzmann factor, leading to the charge density

$$\rho_q(r \geq a) = q\rho_f \exp[-\beta q\psi_n(r)] - \sum_{n=0}^Z (Z-n)q\rho_n + \sigma_n \delta(r-a) , \quad (6)$$

where $\beta^{-1} = k_B T$ and $\psi_n(r)$ is the electrostatic potential at a distance r from the center of the polyion. Notice that only the free counterions are assumed to get polarized; the bare polyions and clusters are too massive to be affected by the electrostatic fluctuations and contribute only to the neutralizing background. Substituting the charge density into the Poisson equation,

$$\nabla^2 \psi_n(r) = -\frac{4\pi}{D} \rho_q(r) , \quad (7)$$

one obtains the nonlinear Poisson-Boltzmann equation. After the linearization of the exponential factor in (6), the electrostatic potential $\psi_n(r)$ satisfies the Laplace (for $r < a$) and the Helmholtz (for $r \geq a$) equations,

$$\nabla^2 \psi_n(r) = \begin{cases} 0 , & \text{for } r < a , \\ \kappa^2 \psi_n(r) - \frac{4\pi}{D} \sigma_n \delta(r-a) , & \text{for } r \geq a , \end{cases} \quad (8)$$

where $\kappa = \sqrt{4\pi\lambda_B\rho_f}$ is the inverse Debye screening length, and $\lambda_B = \beta q^2/D$ is the Bjerrum length. In principle the linearization is valid only in the limit $\beta q\psi_n \ll 1$, however, since the formation of clusters is taken into account, the validity of the theory is extended into the nonlinear regime [3].

The second-order differential equation for $\psi_n(r)$ can be integrated, supplemented by the boundary conditions of vanishing of the electrostatic potential at infinity, the continuity of $\psi_n(r)$ at $r = a$, and the discontinuity in the radial component of the electric field related to the presence of the surface charge σ_n at $r = a$. Under these conditions, we obtain

$$\psi_n(r) = \begin{cases} -\frac{(Z-n)q}{Da(1+\kappa a)} , & \text{for } r < a , \\ -\frac{(Z-n)qe^{\kappa(a-r)}}{Dr(1+\kappa a)} , & \text{for } r \geq a . \end{cases} \quad (9)$$

Using the charge density in the linearized form,

$$\rho_q(r) = \begin{cases} 0 , & \text{for } r < a , \\ -\frac{\kappa^2 D}{4\pi} \psi_n(r) + \sigma_n \delta(r-a) , & \text{for } r \geq a , \end{cases} \quad (10)$$

the electrostatic energy of a n -cluster is calculated to be

$$\begin{aligned} U_n(\kappa, q) &= \frac{1}{2} \int d^3\mathbf{r} \rho_q(r) \psi_n(r) \\ &= \frac{(Z-n)^2 q^2}{D(1+\kappa a)} \left[\frac{1}{a} - \frac{\kappa}{2(1+\kappa a)} \right]. \end{aligned} \quad (11)$$

The electrostatic free-energy density for the polyion-counterion interaction is obtained through the Debye charging process, in which all the particles are simultaneously charged from 0 to their final charge [5],

$$\begin{aligned} \beta f^{\text{PC}}(\rho_f, \{\rho_n\}) &= - \sum_{n=0}^Z \rho_n \int_0^1 d\lambda \frac{2\beta U_n(\lambda\kappa, \lambda q)}{\lambda} \\ &= - \sum_{n=0}^Z \frac{(Z-n)^2 \lambda_B}{2a(1+\kappa a)} \rho_n. \end{aligned} \quad (12)$$

IV. THE POLYION-POLYION INTERACTION

Due to the large asymmetry between the polyions and the counterions, the degrees of freedom associated with the counterions can be effectively integrated out. The long-ranged interaction between two clusters will be screened by the cloud of free counterions, producing an effective short-ranged potential of a DLVO form [9,10],

$$V_{nm}^{\text{eff}}(r) = q^2(Z-n)(Z-m) \frac{\exp(2\kappa a - \kappa r)}{Dr(1+\kappa a)^2}. \quad (13)$$

The *polyion-polyion* contribution to the Helmholtz free energy can then be calculated in the spirit of the usual van-der-Waals theory [3,7a],

$$\begin{aligned} \beta f^{\text{PP}}(\rho_f) &= -\frac{1}{2} \sum_{n=0}^Z \sum_{m=0}^Z \beta \rho_n \rho_m \int d^3\mathbf{r} V_{nm}^{\text{eff}}(r) \\ &= -2\pi \lambda_B \frac{(1+2\kappa a)}{\kappa^2 (1+\kappa a)^2} \sum_{n=0}^Z \sum_{m=0}^Z (Z-n)(Z-m) \rho_n \rho_m = -2\pi \lambda_B \frac{(1+2\kappa a)}{\kappa^2 (1+\kappa a)^2} \rho_f^2. \end{aligned} \quad (14)$$

V. THE COUNTERION-COUNTERION INTERACTION

The *counterion-counterion* contribution, originating from the interactions between the *free* counterions, is calculated using the One Component Plasma (OCP) theory [11]. The electrostatic free energy is found through a Debye charging process and a closed analytic form for $f^{\text{CC}}(\rho_f)$, valid over a wide range of densities, is presented in [11b],

$$\beta f^{\text{CC}}(\rho_f) = -\rho_f \mathcal{F}_{\text{corr}}(\rho_f), \quad (15)$$

$$\begin{aligned} \mathcal{F}_{\text{corr}}(\rho_f) &= \frac{1}{4} \left[1 + \frac{2\pi}{3\sqrt{3}} + \ln \left(\frac{\omega^2 + \omega + 1}{3} \right) - \omega^2 \right. \\ &\quad \left. - \frac{2}{\sqrt{3}} \tan^{-1} \left(\frac{2\omega + 1}{\sqrt{3}} \right) \right], \end{aligned} \quad (16)$$

$$\omega = \omega(\rho_f) = \left\{ 1 + 3 \left[4\pi \lambda_B^3 \rho_f \right]^{1/2} \right\}^{1/3}. \quad (17)$$

In the bulk this contribution is very small, and is included only for completeness.

VI. THE MIXING FREE ENERGY

The mixing free energy reduces to a sum of ideal-gas terms,

$$\beta f^{\text{mix}}(\rho_f, \{\rho_n\}) = \sum_s \rho_s \left[1 - \ln \left(\rho_s \Lambda_s^3 / \zeta_s \right) \right], \quad (18)$$

where $s \in \{f; n = 0, \dots, Z\}$, Λ_s are the thermal de Broglie wavelengths associated with free counterions, bare polyions, and clusters; ζ_s are the internal partition functions for an isolated specie s . Since the bare polyions and the free (unassociated) counterions do not have internal structure, their internal partition functions are simply given by $\zeta_0 = \zeta_f = 1$. For a n -cluster the internal partition function is

$$\zeta_n = \frac{1}{n!} \int_{\Omega_n} \prod_{i=1}^n \left(\frac{d^3\mathbf{r}_i}{\Lambda_c^3} \right) \exp(-\beta \mathcal{H}_n), \quad (19)$$

$$\beta \mathcal{H}_n = -Z \lambda_B \sum_{i=1}^n \frac{1}{|\mathbf{r}_i|} + \lambda_B \sum_{i < j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (20)$$

where the integration hypervolume $\Omega_n \equiv \{a < |\mathbf{r}_i| < R_n, \forall i = 1, \dots, n\}$ depends on the cutoff R_n . To fix the value of the cutoff, we follow an argument similar to the one used by Bjerrum in his study of dipolar formation in simple electrolytes [4]. Suppose that we have a $(n-1)$ -cluster and we want to condense one more counterion to form a n -cluster. Because of the spherical symmetry, the $(n-1)$ bound counterions contribute only to the renormalization of the polyion charge. The probability of finding the n^{th} counterion at a distance r in the interval dr is

$$\begin{aligned} P(r) dr &\propto dr r^2 \exp[-\beta q\phi(r)] \\ &= dr r^2 \exp[(Z-n+1)\lambda_B/r], \end{aligned} \quad (21)$$

where $\phi(r)$ is the electrostatic potential generated by the $(n-1)$ -cluster. The probability distribution $P(r)$ has a minimum at

$$r = R_n = (Z-n+1) \frac{\lambda_B}{2}, \quad (22)$$

which, following Bjerrum [4], we shall interpret as the distance of closest approach at which the n^{th} counterion will become bound to the $(n-1)$ -cluster. Since $R_n/a > 1$, for a given reduced temperature, $T^* = a/\lambda_B$, there is a minimum value of the valence, $Z_{\min} = 2T^* - 1$, below which no counterions can condense onto a polyion, that is, the thermal entropic energy, $2k_B T$, will overcome the gain in electrostatic potential energy, $(Z-n+1)q^2/(Da)$, preventing the confinement from taking effect.

$$\begin{aligned} \beta\mathcal{F}_n^{\text{con}}[\varrho_c(\mathbf{r})] &= \int_{V_n} d^3\mathbf{r} \varrho_c(\mathbf{r}) \{ \ln [\varrho_c(\mathbf{r})\Lambda_c^3] - 1 \} - Z\lambda_B \int_{V_n} d^3\mathbf{r} \frac{\varrho_c(\mathbf{r})}{|\mathbf{r}|} + \frac{1}{2}\lambda_B \int_{V_n} d^3\mathbf{r} d^3\mathbf{r}' \frac{\varrho_c(\mathbf{r})\varrho_c(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \\ &+ \int_{V_n} d^3\mathbf{r} \varrho_c(\mathbf{r}) \mathcal{F}_{\text{corr}}[\varrho_c(\mathbf{r})], \end{aligned} \quad (24)$$

where the integrations are over the annulus $V_n \equiv \{a \leq |\mathbf{r}| \leq R_n\}$ and $\mathcal{F}_{\text{corr}}$ is given by Eq. (16). The first term in (24) corresponds to the usual ideal-gas contribution, the second and the third terms are due to the electrostatic interactions and the last term is the result of the correlations between the bounded counterions, for which we use the expression of the OCP theory [11]. The equilibrium configuration, $\rho_c(\mathbf{r}) = \langle \varrho_c(\mathbf{r}) \rangle$, is the one that minimizes the free-energy functional $\beta\mathcal{F}_n^{\text{con}}[\varrho_c(\mathbf{r})]$ under the constraint

$$\int_{V_n} d^3\mathbf{r} \rho_c(\mathbf{r}) = n. \quad (25)$$

This minimization procedure leads to the Boltzmann distribution for the density profile,

$$\rho_c(\mathbf{r}) = \frac{n \exp[-\mu_{\text{corr}}(\mathbf{r}) - \beta q\psi(\mathbf{r})]}{\int_{V_n} d^3\mathbf{r}' \exp[-\mu_{\text{corr}}(\mathbf{r}') - \beta q\psi(\mathbf{r}')]}, \quad (26)$$

where the electrostatic and the excess chemical potentials are given, respectively, by

$$\psi(\mathbf{r}) = -\frac{Zq}{D|\mathbf{r}|} + q \int_{V_n} d^3\mathbf{r}' \frac{\rho_c(\mathbf{r}')}{D|\mathbf{r}-\mathbf{r}'|}, \quad (27)$$

$$\begin{aligned} \mu_{\text{corr}}(\mathbf{r}) &= \mathcal{F}_{\text{corr}}[\rho_c(\mathbf{r})] + \rho_c(\mathbf{r}) \frac{\delta\mathcal{F}_{\text{corr}}[\rho_c(\mathbf{r})]}{\delta\rho_c(\mathbf{r})} \\ &= \mathcal{F}_{\text{corr}}[\rho_c(\mathbf{r})] + \frac{1}{12} \{1 - \omega^2[\rho_c(\mathbf{r})]\}, \end{aligned} \quad (28)$$

with ω given by Eq. (17). On the other hand, the electrostatic potential and the total charge density satisfy the Poisson equation,

With the cutoff defined, we shall now attempt to calculate the internal partition function of a n -cluster, Eq. (19). That, in itself, is a formidable task, since it requires evaluation of the many-body integrals (19). Instead of performing the integrations explicitly, we shall use the local-density-functional theory to find the free energy of the condensed layer of n counterions, $\beta F_n^{\text{con}} \equiv -\ln \zeta_n$. Let us define the local density of counterions in the condensed layer of a n -cluster as

$$\varrho_c(\mathbf{r}) = \sum_{i=1}^n \delta(\mathbf{r} - \mathbf{r}_i). \quad (23)$$

Within the local-density approximation (LDA), the Helmholtz free-energy functional $\beta\mathcal{F}_n^{\text{con}}[\varrho_c(\mathbf{r})]$ corresponding to density $\varrho_c(\mathbf{r})$ is

$$-\nabla^2\psi(\mathbf{r}) = \nabla \cdot \mathbf{E}(\mathbf{r}) = \frac{4\pi}{D} [\sigma_0 \delta(|\mathbf{r}| - a) + q\rho_c(\mathbf{r})], \quad (29)$$

where $\mathbf{E}(\mathbf{r}) = -\nabla\psi(\mathbf{r})$ is the electric field at the point \mathbf{r} . Inserting (26) into (29) we find a Poisson-Boltzmann-like equation, which is a second-order nonlinear differential equation for the electrostatic potential $\psi(\mathbf{r})$. It should be remarked that, neglecting the correlation term, we regain the usual Poisson-Boltzmann equation, $\nabla^2\psi(\mathbf{r}) \propto \exp[-\beta q\psi(\mathbf{r})]$.

Since the boundary conditions are given in terms of the electric field strength,

$$E(|\mathbf{r}| = a) = -\frac{Zq}{Da^2} \quad \text{and} \quad E(|\mathbf{r}| = R_n) = -\frac{(Z-n)q}{DR_n^2}, \quad (30)$$

to perform the numerical calculations it is convenient to rewrite the equations in terms of this variable. We now take advantage of the spherical symmetry of the system to eliminate the angular dependence of the equations, that is, we replace \mathbf{r} by $r = |\mathbf{r}|$ in Eqs. (26) to (29). The electric field also has only a spherically symmetric radial component, so that $\mathbf{E}(\mathbf{r}) = E(r) \frac{\mathbf{r}}{r}$. Integrating the Poisson equation (29) over a sphere of radius r and using the divergence theorem, we obtain a relation for the electric field strength $E(r)$,

$$\int_{|\mathbf{r}'| < r} d^3 \mathbf{r}' \nabla \cdot \mathbf{E}(\mathbf{r}') = \int_{|\mathbf{r}'|=r} d\mathbf{S}' \cdot \mathbf{E}(\mathbf{r}') = 4\pi r^2 E(r) = -\frac{4\pi q}{D} \left[Z - \int_{|\mathbf{r}'| < r} d^3 \mathbf{r}' \rho_c(\mathbf{r}') \right]. \quad (31)$$

Inserting (26) into (31) we obtain an integro-differential equation for the electric field,

$$E(r) = -\frac{q}{Dr^2} \left\{ Z - n \frac{\int_a^r dr' r'^2 \exp \left[-\mu_{\text{corr}}(r') + \beta q \int_a^{r'} dr'' E(r'') \right]}{\int_a^{R_n} dr' r'^2 \exp \left[-\mu_{\text{corr}}(r') + \beta q \int_a^{r'} dr'' E(r'') \right]} \right\}, \quad (32)$$

where we have chosen the gauge in which $\psi(r = a) = 0$, and the density profile, $\rho_c(r)$, which is necessary to evaluate $\mu_{\text{corr}}(r)$, is also written in terms of the electric field,

$$\rho_c(r) = \frac{D}{4\pi q} \nabla \cdot \mathbf{E} = \frac{D}{4\pi q r^2} \frac{d}{dr} [r^2 E(r)]. \quad (33)$$

The integro-differential equation was solved iteratively to obtain the electric field $E(r)$. The charge density $\rho_c(r)$ is then calculated using Eq. (33). Finally, the internal free energy of a n -cluster can be expressed in terms of the charge density and the electric field to be

$$\begin{aligned} \beta F_n^{\text{con}} = \beta \mathcal{F}_n^{\text{con}}[\rho_c(r)] &= \int_{V_n} d^3 \mathbf{r} \rho_c(r) \{ \ln [\rho_c(r) \Lambda_c^3] - 1 \} + \frac{\beta D}{8\pi} \int_{V_n} d^3 \mathbf{r} E^2(r) + \frac{(Z-n)^2 \lambda_B}{2R_n} - \frac{Z^2 \lambda_B}{2a} \\ &+ \int_{V_n} d^3 \mathbf{r} \rho_c(r) \mathcal{F}_{\text{corr}}[\rho_c(r)], \end{aligned} \quad (34)$$

while the internal partition function of a n -cluster is $\zeta_n = \exp(-\beta F_n^{\text{con}})$.

VII. THERMODYNAMIC PROPERTIES

The total Helmholtz free energy of the polyelectrolyte solution is a sum of the entropic and the electrostatic contributions,

$$f(\rho_f, \{\rho_n\}) = f^{\text{mix}} + f^{\text{PC}} + f^{\text{PP}} + f^{\text{CC}}. \quad (35)$$

Minimization of the total Helmholtz free energy under the constraints of fixed number of polyions and counterions leads to the law of mass action,

$$\mu_0 + n\mu_f = \mu_n, \quad (36)$$

where the chemical potential of a species s is $\mu_s = -\partial f / \partial \rho_s$. This results in a set of Z coupled nonlinear algebraic equations for the densities ρ_n , whose form is suitable to the use of an iterative method. Starting from a uniform distribution of clusters $\{\rho_n\}$, we were able to solve the coupled system numerically. A sample of the distributions obtained is presented in Fig. 1. Two features are worth remarking. The counterion condensation

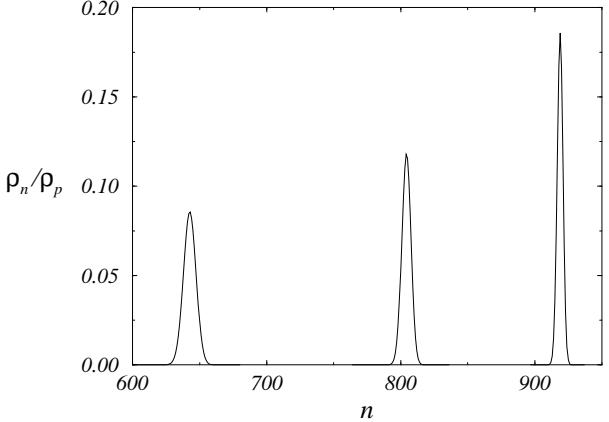


FIG. 1. Cluster-density distribution $\{\rho_n\}$ for $Z = 1000$, volume fraction $\phi = \frac{4}{3}\pi a^3 N_p / V = 0.01$, and various values of temperature. From left to the right, the values of the reduced temperature are $T^* = 100, 50$, and 20 .

is more effective as the temperature decreases, and the width of the distribution is not very sensitive to the variations in temperature. The pressure can be obtained as a Legendre transform of the Helmholtz free-energy density,

$$p = f(\rho_f, \{\rho_n\}) + \sum_s \mu_s \rho_s. \quad (37)$$

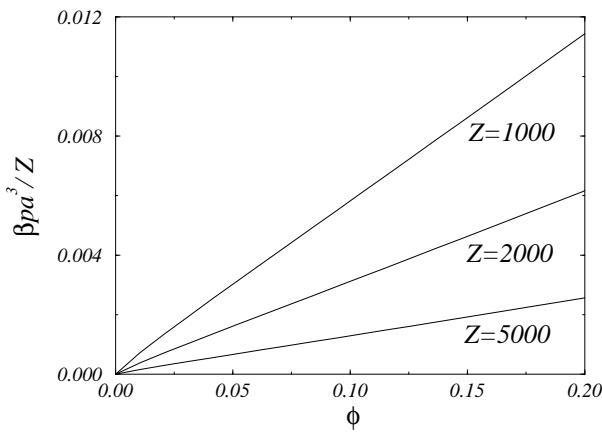


FIG. 2. Dependence of the dimensionless (total) pressure, $\beta p a^3 / Z$, on the volume fraction $\phi = \frac{4}{3} \pi a^3 N_p / V$, for several values of Z (1000, 2000, 5000) and $T^* = 100$.

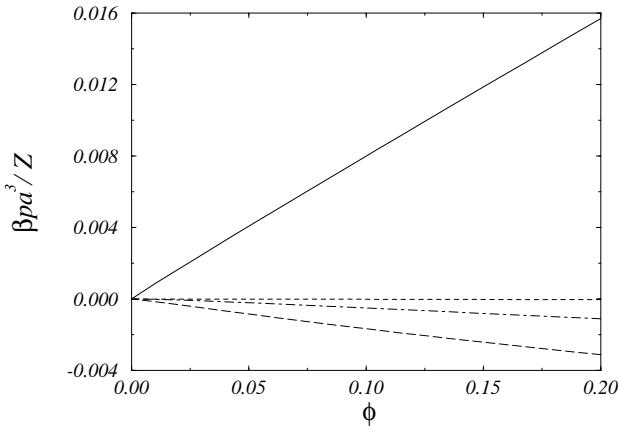


FIG. 3. Dependence of the various contributions to the dimensionless (total) pressure, $\beta p a^3 / Z$, on the volume fraction $\phi = \frac{4}{3} \pi a^3 N_p / V$, for $Z = 1000$, and $T^* = 100$. Solid line: mixing (ideal-gas) contribution; long-dashed line: polyion-counterion contribution; dot-dashed line: polyion-polyion contribution; dashed line: counterion-counterion contribution.

In Fig. 2 we present the total pressure inside the polyelectrolyte solution, which is a monotonically increasing function of the density of polyions. In agreement with the current experimental and Monte Carlo results [12], no evidence of any phase transition is encountered. To allow for a better appreciation of the relative importance of all the terms, in Fig. 3 we present separately the various contributions to the total pressure. All the electrostatic terms give a *negative* contribution to the total pressure, what can be interpreted as a form of an induced effective attraction between all the particles.

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